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Impact of Stainless Steel-Carbon Steel Galvanic Corrosion on Tank Closure and Tank Lifetime Analysis

Executive Summary

The carbon steel primary wall is credited as a barrier for the F-Area and H-area performance assessments [1, 2]. Corrosion is the primary degradation mechanism considered for this barrier. Therefore, any change in the configuration that was assumed by the performance assessment must be evaluated as to its impact on the corrosion rates. Due to physical constraints, stainless steel equipment utilized during the closure of waste tanks may remain on the bottom of the tank. Contact

between the stainless steel equipment and the low-carbon steel tank in certain environments can result in galvanic corrosion. The degree of corrosion depends on the environment and the relative amount of surface area contacted. In general, stainless steel is more noble to carbon steel and the result is that the carbon steel will corrode at an accelerated rate. One method to determine if the stainless steel equipment will affect the anticipated tank lifetime is to compare the galvanic corrosion rate for the carbon steel to the corrosion rate used to calculate tank lifetime. This report examines whether the presence of the SS equipment would reduce the failure times below estimates in the performance assessments for the F-tank farm and the H-tank farm.

It was determined that the galvanic corrosion rates were lower than the assumed average corrosion rate for the tanks and approximately 10 times below the maximum rate assumed during stochastic modeling. Mitigating factors that reduce the anticipated galvanic corrosion were identified. The combination of a corrosion rate well within the range for the stochastic modeling and that will likely be below the 0.04 mpy average rate used in deterministic corrosion modeling led to a conclusion that closing any tank with stainless steel equipment on the bottom will be safe.

Introduction

Due to physical constraints, it is desired to leave some stainless steel (SS) material in the waste tanks during the closure process for waste tanks in the F-area and H-area tank farms at the Savannah River Site. The list of material to be left in the tank during closure includes, but is not limited to: pumps, remote spraying equipment, and measuring tapes. Since the waste tanks are constructed from low-carbon steel (LCS), the contact with the dissimilar SS equipment can cause galvanic corrosion when it is in contact with an electrolyte solution. Previous reports from the corrosion group at SRNL have examined potential degradation of waste tanks due to galvanic corrosion over periods of months and years when SS equipment is left in the tank. The conclusion in all of the SRNL reports was that galvanic corrosion rate for galvanic coupling of SS and LCS was small enough to be neglected given the criteria in each report. However, the analysis contained in these reports did not consider the long term effect (i.e., thousands of years) of this equipment on the tank lifetime performance assessment. This report examines whether the presence of the SS equipment would reduce the failure times below estimates in the performance assessments (PA) for the F-tank farm and the H-tank farm.

In the performance assessments, there were several periods during tank lifetime that could be affected by galvanic corrosion. These periods include the initial phase where the tank is protected by concrete, after the degradation of the concrete when the tank is exposed to soil, and after events such as the formation of a humid air pipe. It is anticipated that the primary galvanic corrosion effect from the equipment would occur during the early tank life when the tank is fully protected from the external environment by concrete and where the overall corrosion rate is relatively low, however other scenarios will be discussed.

Analysis

The report WSRC-TR-2004-00580 [3] details experiments performed to determine the corrosion rate for the LCS waste tanks. The conclusion from the testing was that in all cases the galvanic corrosion should be less than 1 mil per year (mpy) based on direct measurements using a zero-resistance ammeter and indirect measurements using an overlay technique with cyclic potential polarization results for the individual. The performance assessments for the F-tank farm (WSRC-STI-2007-00061 [1]) and the H-tank farm (SRNS-STI-2010-00047 [2]) both used a corrosion rate of 0.04 mpy as the corrosion rate for the tanks while the concrete vault is still intact. The 1 mpy value listed in the conclusions of WSRC-TR-2004-00580 is significantly larger than the 0.04 mpy corrosion rate for passive carbon steel. Therefore, additional analysis of the experiments and anticipated conditions in the tank are needed to determine whether there might be a risk of premature waste tank degradation compared to the PA tank lifetimes.

The examination of the galvanic corrosion results focused on the two methods that were used to estimate a corrosion rate for the LCS tanks. The direct measurement method using a zero-resistance ammeter bears the most similarities to the conditions in the tank. When using the zero resistance ammeter, two metals coupons are kept in close contact with a thin layer of electrical insulation between them and electrical contact is made through an external wire that is in series with the ammeter. The galvanic couple is immersed in electrolyte and the galvanic corrosion current is measured as the electrochemical reaction occurs. The indirect measurement using the overlay method carries out cyclic potentiodynamic polarization or tafel plots for both metals individually in the same solution and then determines the corrosion current from a plot where the two curves are plotted simultaneously. The corrosion potential and current occur at the point where the cathodic scan from the corrosion potential of the more noble metal (SS) intercepts the anodic scan from the corrosion potential of the more active metal (CS). Figure 1, reproduced from WSRC-TR-2004-00058 [3], illustrates how the overlay method can be used to estimate corrosion current. The plot in Figure 1 is also relevant for the discussion of the different corrosion rate estimation methods because it is for sample #9 which was one of two samples that were tested using both the overlay method and zero-resistance ammeter. The 0.055 $\mu A/cm^2$ current density corresponds to a corrosion rate of 0.03 mpy, which is below the corrosion rate for the passive LCS tank.

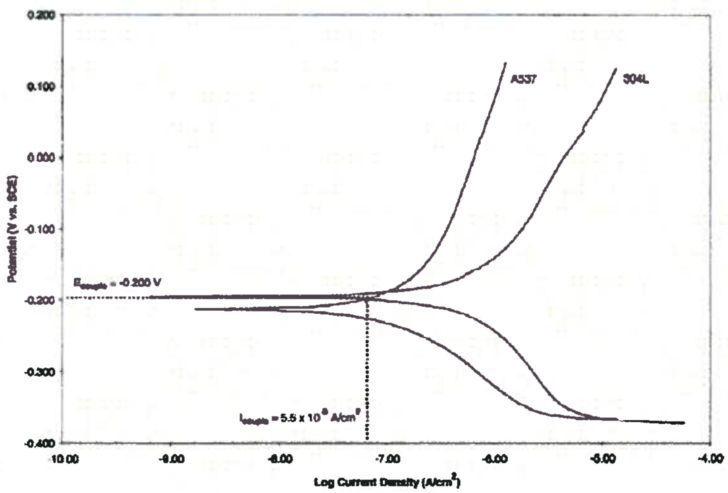

Figure 1. Overlay method for determining corrosion potential and corrosion current. Reproduced from WSRC-TR-2004-00058 (Sample 9) [3].

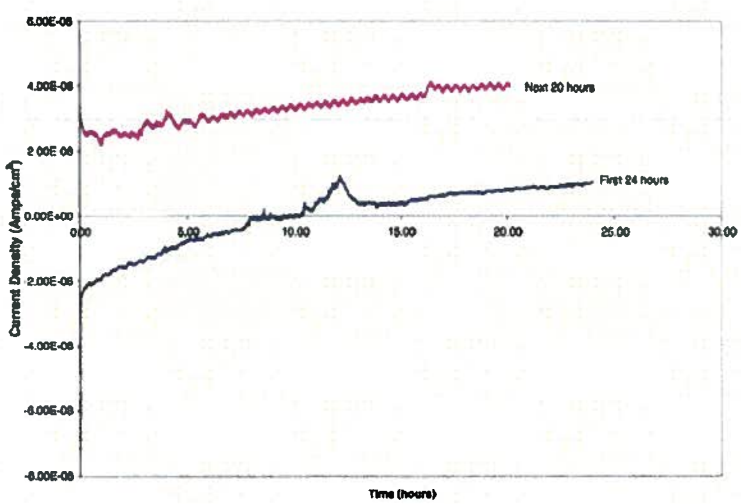

Figure 2. Corrosion current density measured by a zero resistance ammeter over 44 hours. Reproduced from WSRC-TR-2004-00058 (Sample 10) [3].

For sample 10, the corrosion current measured by a zero-resistance ammeter is shown in Figure 2. After 44 hours in the solution, the corrosion current density was 0.040 $\mu A/cm^2$ or 0.02 mpy. Similar tests conducted for sample 9 had cathodic currents for the LCS with an equivalent corrosion rate of 0.006 mpy for SS after 24 hours. Although the cathodic currents indicate initial corrosion of the stainless steel, it is anticipated that after sufficient time the corrosion currents for the LCS would have turned anodic. However, it is also expected that the corrosion rate of the LCS under these conditions would be very low.

Comparing the zero-resistance ammeter data and the overlay data for the samples where both experiments were performed shows that the direct measurement of the corrosion current is significantly lower than the corrosion current density estimated by the overlay method. The difference in corrosion rates between the two methods may be due to more steady-state polarization behavior over long periods of time for zero-resistance ammeter tests as compared to a fixed rate scan for Tafel or cyclic potentiodynamic polarization experiments that includes some capacitive currents in the total current. Although capacitive currents can generally be neglected for slow scan rates they may be significant with small corrosion currents close to the corrosion potentials. Also, the corrosion potential of the couple may be different from the overlay method due to effects of reaction products in solution near the samples or depletion of reactants near the metal surface that forms a protective diffusion layer. The testing conditions for the zero-resistance ammeter tests should be more realistic to the corrosion process in waste tanks over long periods of time when compared to the overlay method. Therefore, it is recommended to use the zero-resistance ammeter measurements when determining the significance of galvanic corrosion.

Literature results were surveyed to compare our observations and experimental results. A paper by Abreu from 2002 [4] provides additional evidence about the magnitude of galvanic corrosion between LCS and SS in basic solutions. Figure 3 shows results from Abreu et al. that has corrosion currents of similar magnitude to those observed in experiments at SRNL. The results also provide additional support for the use of zero-resistance ammeter data to quantify corrosion rates for galvanic corrosion rates. The galvanic corrosion rates below 0.04 mpy from direct experiments indicate galvanic corrosion should not change the conclusions of the PA for the F-tank farm and H-tank farm.

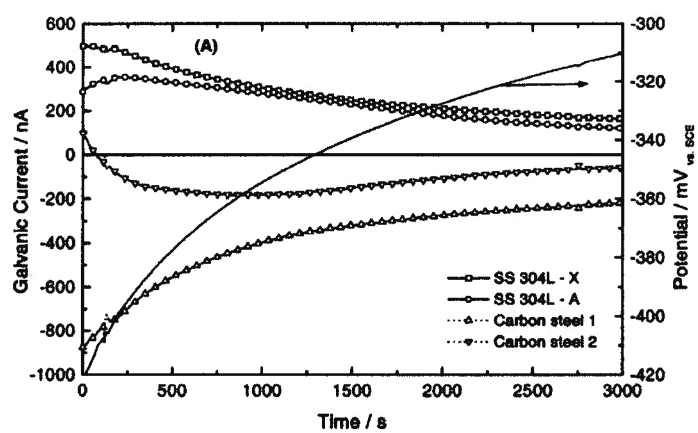

Figure 3. Galvanic corrosion currents using a zero-resistance ammeter between stainless steel and carbon steel in a 0.01 M NaOH solution. Reproduced from Abreu, et al. 2002 [4].

Although the low zero resistance ammeter corrosion rates provide strong evidence that the tanks will be passive when in contact with stainless steel, there are numerous additional mitigating factors that should decrease galvanic corrosion from the values outlined above:

1. The surface area of the low-carbon steel tanks is orders of magnitude larger than the total surface area of the all the stainless steel equipment within the tanks. The galvanic corrosion

experiments were performed with a 1:1 area ratio for the LCS and SS. Since the corrosion current will be spread over the entire reaction area that is in contact with the electrolyte, the corrosion current density for the low-carbon steel tanks will be significantly lower than the current densities estimated in the corrosion experiments. This will be the main mitigating factor for the galvanic corrosion due to the magnitude of the difference in the relative areas of the tank and the SS equipment.

2. The corrosion experiments assume that the reaction surfaces have no adsorbed films and are completely open to the electrolyte. Also, it is assumed that the electrolyte has an unobstructed path between the metals. In actuality, the tank will be filled with a grout that will likely adsorb on the metal surfaces and the grout will have a low porosity through which the electrolyte can flow.
3. The experiments at SRNL were performed at 45°C, but after the concrete finishes curing it is anticipated that the tanks should be at temperature of the soil surrounding the tanks. This soil is estimated to be at 10°C most of the year. If it is assumed that the reaction rate is decreased 50% for every 10°C decrease in temperature, then the long-term galvanic corrosion rate should be over 8 times lower than results at 45°C. This means that the main corrosion rate risk will be during the initial curing of the concrete when it can reach temperatures of 65°C [5].
4. Corrosion experiments have samples with good electrical connections. In the tanks, the electrical conductivity could be reduced due to oxide layers and corrosion products on metallic surfaces. Additionally, there may be contact resistance due to uneven surfaces. The ohmic losses from these factors could reduce polarization of the metals and thereby reduce galvanic corrosion.

Although it is difficult to fully quantify the effect of all mitigating factors on the galvanic corrosion rate of the waste tanks due to the presence of stainless steel equipment, the decrease in the corrosion current density compared to the zero-resistance ammeter tests in WSRC-TR-2004-00580 [3] should be significant. Given the already low corrosion rates of approximately 0.02 mpy at 45°C, it is anticipated that the galvanic corrosion of the tanks due to the SS equipment will be negligible and below 0.04 mpy for all cases. There may be slightly higher corrosion rates during curing of the grout that may elevate temperatures to 65°C [5], but it is anticipated that these will dissipate within months of closure and would not be high enough to cause damage to the tank due to its large size.

The full stochastic models for the F-tank farm and H-tank farm also considered the possibility that the average corrosion rate for the waste tanks was above the value of 0.04 mpy. In the F-tank farm model, the upper limit for the corrosion rate was 0.44 mpy although the probability of this elevated rate occurring was very low. In the distribution of corrosion rates, 0.04 mpy was approximately the median value with half of the corrosion rates above this value. Even with the possibility of having these elevated corrosion rates, there was little concern about premature tank failure. Similar full stochastic analyses were performed in the H-tank farm PA and the corrosion rates started at 0.04

mpy and went up to 1.1 mpy. The corrosion rate range went up to higher values for the H-tank farm due to the potential for changing of the groundwater level.

Conclusions

It has been recognized for several years at SRNL that the use of stainless steel submersible pumps and other stainless steel equipment within low-carbon steel waste tanks has the potential to cause galvanic corrosion. Previous analysis of the corrosion risk posed by galvanic corrosion of the LCS and SS couple has concluded that in all cases the corrosion will be less than 1 mpy. However, a more specific analysis for the effect of galvanic corrosion during closure where corrosion rates of 0.04 mpy has not been performed. This report analyzed the experimental results more closely and has found that zero-resistance ammeter measurements of galvanic corrosion have shown that corrosion rates will be below 0.02 mpy at temperatures as high as 45°C. In addition, multiple mitigating factors were identified that should reduce the corrosion rate significantly from these values. The ability of the full stochastic model in the performance assessments to account for a large increase in the corrosion rate was also discussed. Based on this analysis, it has been concluded that leaving the stainless steel material is in waste tanks does not necessitate changes to the corrosion rate inputs for the performance assessments for the F-tank farm or the H-tank farm.

References

1. Subramanian, K.H., *Life Estimation of High Level Waste Tank Steel for F-Tank Farm Closure Performance Assessment, Rev.2*, WSRC-STI-2007-00061, Rev. 2, 2007.
2. Garcia-Diaz, B.L., *Life Estimation Of High Level Waste Tank Steel For H-Tank Farm Closure Performance Assessment*, SRNS-STI-2010-00047, 2010.
3. Wiersma, B.J. and J.I. Mickalonis, *Galvanic Corrosion In Waste Tank Environments*, WSRC-TR-2004-00580, 2004.
4. Abreu, C.M., et al., *Galvanic coupling between carbon steel and austenitic stainless steel in alkaline media.* Electrochimica Acta, 2002. **47**(13-14): p. 2271-2279.
5. Chander, V., *Develop Tank Closure Technology Grout Formulations for Tanks 18 and 19*, HTE-TTR-2011-008, 2011.